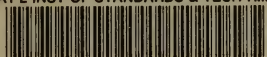


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## THE SPECTRA OF MIXED GASES.

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Early in spectroscopic work it was observed that mixed gases frequently gave the spectrum of a heavy metallic component more strongly than that of a lighter component. In 1878 E. Wiedemann<sup>a</sup> described experiments with mercury and sodium in hydrogen and nitrogen. He proved that the intensities of the metallic spectra were out of all proportion to the relative amounts of metallic vapor present. It is a matter of common experience in preparing Plücker tubes to exhibit metallic spectra that as soon as the tube is heated sufficiently to vaporize the contained metal, the spectrum of the lighter gas filling the tube disappears. Recently Professor Lewis has shown<sup>b</sup> that when mercury vapor is present in a tube of hydrogen it will reduce the hydrogen spectrum to about half its original intensity when but one molecule of mercury to three thousand of hydrogen are present. It is well known that the cadmium spectrum will swamp that of hydrogen long before the cadmium is even melted. The red lines of the two spectra are equal at a temperature of about 200° C.

At first thought we should say in explanation that the vapor of a metal would be a better electrical conductor than that of a nonmetal, and, carrying the most of the current, would show the brightest spectrum. But this hypothesis is clearly untenable. Although gas conductivities have not yet been accurately determined nor yet even defined, it is well known that under the same conditions metallic vapors do not differ widely from nonmetallic vapors and the permanent gases in conducting power. And even then, why should the vast majority of lighter molecules be left idle as soon as a few of the heavier molecules are present?

Taking up the problem at this point, it was quickly shown that metallic character has little if anything to do with spectral predominance. Sulphur and iodine are nearly as effective in swamping

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<sup>a</sup> E. Wiedemann: *Wied. Ann.*, 5, pp. 500-524; 1878.

<sup>b</sup> P. Lewis: *Astroph. J.*, 10, pp. 137-163; 1899. *Ann. d. Phys.*, 2, pp. 447-458; 1900.

hydrogen and nitrogen as are mercury and cadmium. Further, a nonmetallic vapor may swamp a metallic. This was shown by a combination of sodium with bromine and iodine vapors. Iodine was found to be much more effective than chlorine, and this suggested that atomic weight might be the ruling factor. This view was confirmed by all the evidence obtained. Even the persistent mercury spectrum may be displaced by the slightly heavier thallium, iodine easily swamps chlorine and sulphur, while any of the heavier metals displaces sodium, itself so persistent in lighter gases. In all, about eighty combinations of the fifteen available vaporizable elements were tested without any contradictions to the atomic weight law being discovered; but several combinations like cadmium and indium, oxygen and nitrogen, of elements of nearly equal atomic weight would require a more accurate determination of relative pressure and spectral energy to be used in evidence. The law may be stated thus: In the spectrum of a mixture of gases, other things being equal, *the spectrum of the gas of greater atomic weight will be brighter*. This applies to such simple, moderate, fairly homogeneous excitation as we have in a Plücker tube containing gases under a pressure of from 0.1 mm to 10 mm carrying a current of not more than 10 milliamperes. Outside these limits, the atomic-weight effect is always less—i. e., the intensities of the spectra are more nearly in proportion to the relative amounts of the gases present. With excessive excitation, say with more than one-twentieth microfarad capacity in parallel with the tube of gas, secondary spectra are produced and the relative intensity of secondary spectra appears to depend only on the relative numbers of the two kinds of atoms present. In the luminous portions of the arc and spark, conditions of pressure, current density, etc., are so complex that a test is almost hopeless, but there are many indications that the atomic-weight law of spectral partition holds here as well.

The greater part of the work here described was done with small Plücker tubes excited by a 2,000-volt alternating current. Sometimes a small induction coil was used. Tests of easily vaporizable substances were repeated with tubes having external electrodes. Other tests were repeated with small electrodeless tubes excited by electric waves from a Seibt quarter wave resonance apparatus. Spectra were examined with a small direct vision spectroscope. On account of the greater ease in identifying and comparing spectra, a low dispersion is preferable. Except in a few instances, the effects to be observed were so pronounced that no accurate photometry nor measurements of the relative amounts of gases present were necessary. Sometimes the two spectra were brought to equality and relative pressure estimated, and



sometimes the tube was filled with nearly equal quantities of the two vapors and relative spectral energies estimated. A list of the tests made is given below. A plus sign indicates that tests were made and that the results obtained confirmed the atomic weight law. A parenthesis indicates that more accurate measurements of pressure and spectral energy are necessary to decide spectral predominance for equal proportions. Where spaces are left blank no tests were made.

At. wt.	El	Tl	Hg	I	Te	In	Cd	Br	Se	Zn	Cl	S	Na	O	N
1.....	H	+	+	+	+	+	+	+	+	+	+	+	+	+	+
14.....	N	+	+	+	+	+	+	+	+	+	+	+	+	(+)	
16.....	O	+	+				+				(+)	+	+		
23.....	Na		+	+	+	+	+	+	+	+	+				
32.....	S	+	+	+	+	+	+	+	+	+	(+)				
35.....	Cl	+	+	+			+	+							
65.....	Zn	+	+				+								
79.....	Se	+	+	+	+	+	+								
80.....	Br	+	+	+			+								
112.....	Cd	+	+	+		(+)									
114.....	In	+	+	+											
125.....	Te														
127.....	I	+	+												
200.....	Hg	(+)													
204.....	Tl														

In addition to these results may be cited the work of Collie and Ramsay<sup>a</sup> on mixtures of argon and helium. They found that a little argon mixed with helium showed the spectrum of the former strongly, while a small percentage of helium in argon showed but a faint helium spectrum.

Chemical combination occurs in the vast majority of cases, but compound spectra occur only in the case of a few halides. Chemical combination, however, appears to have no effect on the relative spectral energies of the components, just as though the electrical excitation in all cases produces a completely nascent state of each atom before luminescence occurs. If we start with, say, hydrogen and sulphur, vaporize the sulphur and then allow the tube to cool while the discharge is passing, we get no spectrum other than those of hydrogen and sulphur during the process, and no trace of  $H_2S$  on opening the tube. The result is the same when we fill the tube with  $H_2S$  at the start. Similarly with black mercury sulphide, except that a heavy deposit of sulphide remains. Even with the cadmium-oxygen combination, where the product can not be kept vaporized, the two spectra may be observed superposed during combination. But with the

<sup>a</sup>Proc. Roy. Soc., 59, pp. 257-270; 1896.

mercury halides a strong band appears, brighter even than the mercury spectrum. The halogen spectrum remains visible as well as the mercury, evidently in proportion to the atomic weights of these substances, but the compound spectrum is brighter than either, possibly in proportion to the molecular weight of the compound. It would be in accord with theory if the spectra of compounds followed a molecular weight law, but too few compound spectra exist to give it much weight. Varying the pressure over quite a range does not generally affect the preponderance of one spectrum over another. But at very high or very low pressure the spectrum of the lighter gas is stronger in proportion than at intermediate pressures. Changes in temperature have little effect so long as all components and products remain vaporized.

Changes in current density over quite a wide range do not affect the spectral preponderance.<sup>a</sup> But an excessive current density was found to increase the relative intensity of the lighter gas in every case observed. This test was made with some special Plücker tubes having a third bulb in the middle of the capillary. Though the central bulb had several hundred times the cross section of the neighboring capillary the spectra of the two portions never differed greatly. Excessive current density of course produces an excessive electrical excitation of the atom much as the addition of capacity does. Hence heavy currents tend to produce secondary spectra and hence a division of spectral energy in proportion to the relative numbers of the two kinds of atoms present. The effect of introducing inductance or resistance with the capacity appears to be merely to partly neutralize the effect of the capacity, i. e., to favor the preponderance of the spectrum of the gas of greater atomic weight.

Frequently portions of one spectrum will swamp the nearest lines of the other spectrum first. This effect is most marked in combinations of some metallic vapor with nitrogen or a halogen. Combinations with the sulphur group, however, show no trace of this effect. Thallium appears to weaken the *distant* (red) oxygen lines most.

No attempt at quantitative work has been made, nor any attempt to establish a quantitative relation between spectral preponderance and atomic or molecular weight. Judging by the work here described, relative spectral energy might well be proportional to atomic weight; it certainly is not less but may be more than proportional.

In obtaining pure spectra, then, impurities of high atomic weight are to be particularly avoided. In working with the spectra of gases or vapors of great atomic weight, the presence of impurities

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<sup>a</sup> See Ferry: Phys Rev., 7, p. 305; 1898.



of low atomic weight will be of little consequence. For detecting spectroscopically small amounts of vapors of large atomic weight, the primary spectrum is most favorable. If, however, it is desired to detect a small amount of a light gas mixed with a heavier, it is best to work with secondary spectra.

In conclusion it may be well to call attention to the simple explanation of the phenomena observed afforded by modern theories of gas conduction. Consider a current consisting of a convection of charged particles. Consider luminous and ultra violet radiation as due to vibrations of the electrons composing the atom. Excitation would be due the impact of electrons, largely negative. The larger atoms would not only be hit most frequently, but would shield the smaller atoms from impact by the moving negative electrons. At very low pressures the shielding action would be less in proportion. Irregular heat motion involving atomic and molecular impact would have little effect on either total or relative excitation. Increasing the current would increase the number of exciting electrons and hence the luminosity in proportion. The relative excitation (of large and small atoms) would remain unchanged, while the total excitation would be proportional to the current. While with moderate currents probably but a single electron (if any) is torn from an atom, excessive currents might still further break up the atom and so produce a more and more continuous spectrum. In the rare instances of molecules so stable as to withstand having a fourth of their charge suddenly torn away, the electrons in the combined atoms might still be able to vibrate but with altered and greatly damped vibrations. The large molecules would receive greater excitation than any atoms present. Hence compound spectra, when they do occur, are banded and relatively intense. Oscillating discharges would excite the smaller atoms relatively more than continuous currents.

If the exciting negative electrons are all alike no matter from what atoms they are torn, one can not properly speak of the current being carried by one gas of a mixture more than by another. Distribution of spectral energy would not then be a matter of distribution of current.





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